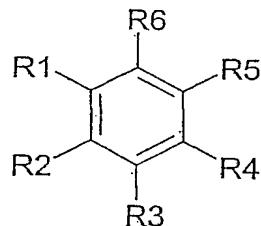


Claims

1. An aqueous acidic solution for electrolytically depositing copper coatings, said solution containing at least one oxygen-containing, high molecular additive and at least one water soluble sulfur compound, characterized in that the 5 solution additionally contains at least one aromatic halogen derivative having the general formula (I)



10

(I)

wherein

15 R_1, R_2, R_3, R_4, R_5 and R_6 are each independently radicals selected from the group comprising hydrogen, aldehyde, acetyl, hydroxy, hydroxalkyl having 1 – 4 carbon atoms, alkyl having 1 – 4 carbon atoms and halogen, with the proviso that the number of radicals R_1, R_2, R_3, R_4, R_5 and R_6 which are halogen ranges from 1 – 5.

20 2. The solution according to claim 1, characterized in that the concentration of the at least one aromatic halogen derivative ranges from about 0.005 – about 0.9 mg/l.

25 3. The solution according to any one of the preceding claims, characterized in that the aldehyde is selected from the group comprising formyl ($-\text{CHO}$), methylformyl ($-\text{CH}_2-\text{CHO}$) and ethylformyl ($-\text{C}_2\text{H}_4-\text{CHO}$).

4. The solution according to any one of the preceding claims, characterized in that alkyl is branched or unbranched and is selected from the group comprising methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl and *tert*-butyl.

5

5. The solution according to any one of the preceding claims, characterized in that alkyl is hydroxyalkyl and that it is branched or unbranched.

6. The solution according to any one of the preceding claims, characterized

10 in that at least one hydroxyalkyl is hydroxymethyl.

7. The solution according to any one of the preceding claims, characterized in that the at least one aromatic halogen derivative is selected from the group comprising

15

2-chlorobenzaldehyde

2-chlorophenol

4-chloro-3-methylphenol

2-chloro-4,5-dimethylphenol

20

4-chloro-3,5-dimethylphenol

4-chlorophenol

3-chlorophenol

o-chloroacetophenone

2-chlorobenzyl alcohol

25

4-bromo-2,6-dimethylphenol

4-bromophenol

2,4-dichlorobenzyl alcohol

2,6-dibromo-4-methylphenol

2,5-dichlorophenol

30

3,5-dibromobenzaldehyde

2,5-dibromobenzoic acid

2,4,6-trichlorophenol

2,3,6-trichlorobenzaldehyde.

8. The solution according to any one of the preceding claims, characterized in that the at least one oxygen-containing, high molecular additive is selected from the group comprising

5 polyvinyl alcohol
carboxymethyl cellulose
polyethylene glycol
polypropylene glycol
stearic acid polyglycol ester
10 oleic acid polyglycol ester
stearyl alcohol polyglycol ether
nonylphenol-polyglycol ether
octanol polyalkylene glycol ether
octanediol-bis-(polyalkylene glycol ether)
5 poly(ethylene glycol-*ran*-propylene glycol)
poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) and
poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol).

20 9. The solution according to any one of the preceding claims, characterized in that the at least one water soluble sulfur compound is selected from the group comprising organic, nitrogen-free thio compounds and the salts thereof.

25 10. The solution according to claim 9, characterized in that the salts contain alkali or earth alkali metal ions, selected from the group comprising sodium, potassium, magnesium and calcium.

11. The solution according to any one of claims 9 and 10, characterized in
30 that the at least one organic nitrogen-free thio compound is selected from the
group comprising

sodium salt of 3-(benzthiazolyl-2-thio)-propylsulfonic acid
sodium salt of 3-mercaptopropane-1-sulfonic acid

disodium salt of thiophosphoric acid-O-ethyl-bis-(ω -sulfopropyl)-ester
trisodium salt of thiophosphoric acid-tris-(ω -sulfopropyl)-ester
sodium salt of ethylenedithio dipropyl sulfonic acid
disodium salt of bis-(*p*-sulfophenyl)-disulfide
5 disodium salt of bis-(ω -sulfopropyl)-sulfide
disodium salt of bis-(ω -sulfopropyl)-disulfide
disodium salt of bis-(ω -sulfohydroxypropyl)-disulfide
disodium salt of bis-(ω -sulfonylbutyl)-disulfide
sodium salt of methyl-(ω -sulfopropyl)-disulfide
10 sodium salt of methyl-(ω -sulfonylbutyl)-trisulfide
potassium salt of O-ethyl-dithiocarbonic acid-S-(ω -sulfopropyl)-ester
thioglycolic acid

12. The solution according to any one of the preceding claims, characterized
15 in that acid is contained in the solution and that the acid is selected from the
group comprising sulfuric acid, hydrochloric acid, fluoboric acid and
methanesulfonic acid.

13. The solution according to any one of the preceding claims, characterized
20 in that the solution additionally contains chloride ions.

14. The solution according to claim 13, characterized in that the chloride ions
have been added to the solution in the form of sodium chloride and/or of
hydrochloric acid.

25 15. The solution according to any one of the preceding claims, characterized
in that the solution additionally contains at least one organic, nitrogen-
containing thio compound.

30 16. The solution according to claim 15, characterized in that the at least one
nitrogen-containing thio compound is selected from the group comprising

thiourea
N-acetylthiourea

N-trifluoroacetyl thiourea
N-ethylthiourea
N-cyanoacetyl thiourea
N-allylthiourea
5 o-tolylthiourea
N,N'-butylene thiourea
thiazolidine thiol-2
4-thiazoline thiol-2
imidazolidine thiol-2-(N,N'-ethylene thiourea)
10 4-methyl-2-pyrimidine thiol
2-thiouracil

17. The solution according to any one of the preceding claims, characterized in that the solution additionally contains at least one polymeric phenazinium 15 compound.

18. The solution according to claim 17, characterized in that the at least one polymeric phenazinium compound is selected from the group comprising

20 poly(6-methyl-7-dimethylamino-5-phenyl-phenazinium sulfate)
poly(2-methyl-7-diethylamino-5-phenyl-phenazinium chloride)
poly(2-methyl-7-dimethylamino-5-phenyl-phenazinium sulfate)
poly(5-methyl-7-dimethylamino-phenazinium acetate)
poly(2-methyl-7-anilino-5-phenyl-phenazinium sulfate)
25 poly(2-methyl-7-dimethylamino-phenazinium sulfate)
poly(7-methylamino-5-phenyl-phenazinium acetate)
poly(7-ethylamino-2,5-diphenyl-phenazinium chloride)
poly(2,8-dimethyl-7-diethylamino-5-p-tolyl-phenazinium chloride)
poly(2,5,8-triphenyl-7-dimethylamino-phenazinium sulfate)
30 poly(2,8-dimethyl-7-amino-5-phenyl-phenazinium sulfate)
poly(7-dimethylamino-5-phenyl-phenazinium chloride)

19. The solution according to any one of the preceding claims, characterized in that the solution additionally contains at least one polymeric nitrogen compound.
- 5 20. The solution according to claim 19, characterized in that the at least one polymeric nitrogen compound is selected from the group comprising polyethylene imine, polyethylene imide, polyacrylic acid amide, polypropylene imine, polybutylene imine, N-methyl polyethylene imine, N-acetyl polyethylene imine, N-butyl polyethylene imine.
- 10 21. Use of the solution according to any one of claims 1 – 20 for depositing a copper coating.
- 15 22. Use of the solution according to any one of claims 1 – 20 for depositing copper onto printed circuit board material.
- 20 23. Use according to any one of claims 21 and 22 for producing copper coatings in vertical and/or horizontal conveyorized plating lines.
24. A method of electrolytically depositing copper coatings on metal or plastic surfaces, comprising bringing the surfaces into contact with the solution according to any one of claims 1 – 20 and electrolytically depositing copper onto the surfaces.